

### Summary

1. The hydrolysis of dimethylketazine has been studied at 15 and at 20° by a kinetic method.
2. The reaction is reversible and an equilibrium is reached involving H<sup>+</sup>, dimethylketazine, acetone hydrazone, acetone and hydrazine.
3. Equilibrium constants have been evaluated under several conditions.
4. The kinetics of the reaction have been studied at the two temperatures and velocity constants for the forward and reverse reactions obtained.
5. Some of the free energy values have been calculated.

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[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE RICE INSTITUTE]

## THE EFFECT OF STRUCTURE OF ORGANIC HALIDES ON THEIR RATE OF REACTION WITH INORGANIC HALIDES.

### III. THE EFFECT OF THE PHENYLTHIO, ALPHA-NAPHTHOXYL AND BETA-NAPHTHOXYL GROUPS

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RECEIVED MAY 4, 1929

PUBLISHED NOVEMBER 8, 1929

Previous papers published from this Laboratory on the effect of structure of organic chlorides on their rate of reaction with potassium iodide in absolute acetone solution have included the effect of the phenoxy and methylthio groups,<sup>1</sup> and it seemed of interest to determine how these rates would be affected by substituting an  $\alpha$ - and  $\beta$ -naphthoxy group for a phenoxy, and a phenylthio group for a methylthio group. The data also give a comparison of the relative effect of an oxygen and sulfur atom in compounds of the structure  $C_6H_5O(CH_2)_nCl$  and  $C_6H_5S(CH_2)_nCl$ . These comparisons are summarized in Table I.

A study of this table brings out the following relationships of structure to reactivity. 1. A chlorine atom in the  $\beta$ -position to a given group has a reactivity which is in every case less than the reactivity of the chlorine atom when in the  $\gamma$ -position to the same group. The ratio of these reactivities at 50° varies between 1:1.53 for the phenyl group, which is the smallest ratio, to 1:6.14 for the  $\alpha$ -naphthyl group, which is the greatest.

2. The temperature coefficient  $A$  is in every case higher in the compounds with two carbon atoms between the chlorine and the activating group than in the corresponding compounds with three carbon atoms. The values for  $A$  in the first case average approximately 4600 and approximately 4150 in the second case.

3. A phenylthio group in the  $\beta$ - or  $\gamma$ -position to a chlorine atom causes the reactivity of that chlorine atom to be about twice as great as when a

<sup>1</sup> Kirner, THIS JOURNAL, 48, 2745 (1926); *ibid.*, 50, 2446 (1928).

TABLE I  
 COMPARATIVE DATA

Compound	$K_{10}$	$K_{30}$	A	Rel. reactivity at 50°, <i>n</i> -butyl chloride as unity
<i>n</i> -C <sub>4</sub> H <sub>9</sub> Cl <sup>a</sup>	0.0415	0.1189	4920	1.00
CH <sub>3</sub> SCH <sub>2</sub> CH <sub>2</sub> Cl <sup>b</sup>	.0629	.1666	4540	1.52
C <sub>6</sub> H <sub>5</sub> SCH <sub>2</sub> CH <sub>2</sub> Cl	.0234	.0639	4706	0.56
C <sub>6</sub> H <sub>5</sub> OCH <sub>2</sub> CH <sub>2</sub> Cl <sup>c</sup>	.0124	.034	4710	0.30
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CH <sub>2</sub> Cl <sup>a</sup>	.0466	.108	3920	1.12
$\alpha$ -C <sub>10</sub> H <sub>7</sub> OCH <sub>2</sub> CH <sub>2</sub> Cl	.0136	.0398	5015	0.33
$\beta$ -C <sub>10</sub> H <sub>7</sub> OCH <sub>2</sub> CH <sub>2</sub> Cl	.0137	.0384	4795	0.33
CH <sub>3</sub> SCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> Cl <sup>b</sup>	.1044	.2373	3830	2.52
C <sub>6</sub> H <sub>5</sub> SCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> Cl	.114	.280	4198	2.74
C <sub>6</sub> H <sub>5</sub> OCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> Cl <sup>c</sup>	.0694	.186	4600	1.67
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> Cl <sup>a</sup>	.0713	.160	3770	1.72
$\alpha$ -C <sub>10</sub> H <sub>7</sub> OCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> Cl	.0835	.205	4200	2.01
$\beta$ -C <sub>10</sub> H <sub>7</sub> OCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> Cl	.0839	.212	4333	2.02

<sup>a</sup> Conant and Kirner, *THIS JOURNAL*, **46**, 235 (1924). <sup>b</sup> From the second paper of this series. <sup>c</sup> From the first paper of this series.

phenoxy group is in the same position. This gives a direct comparison of the effect of the replacement of a sulfur atom by an oxygen atom.

4. The introduction of an oxygen or sulfur atom between the phenyl group and the  $\beta$ -carbon atom (with reference to the chlorine atom) decreases the reactivity of the chlorine atom; but the reactivity of the chlorine is increased if the oxygen or sulfur is introduced between the phenyl group and the  $\gamma$ -carbon atom.

5. The phenylthio group in the  $\beta$ -position to a chlorine atom produces a lower degree of reactivity than a methylthio group, but a greater reactivity when in the  $\gamma$ -position. This is probably what the various theories of alternate polarity would predict on the basis of the greater negativity of the phenyl group compared to the methyl group.

6. An  $\alpha$ - or  $\beta$ -naphthoxy group in the  $\beta$ - or  $\gamma$ -position to a chlorine atom has essentially the same effect as a phenoxy group in the same position, possibly causing a very slightly greater reactivity. There is no detectable difference in the reactivity caused by an  $\alpha$ - or  $\beta$ -naphthoxy group.

The above conclusions are verified in the data collected in Table II, which compares the reactivities of the compounds RCH<sub>2</sub>CH<sub>2</sub>Cl and RCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Cl with ethyl and *n*-propyl chloride, respectively. This table shows the effect of replacing a  $\beta$ -hydrogen in ethyl chloride and a  $\gamma$ -hydrogen in *n*-propyl chloride by an R group. The additional relationship is brought out from this table that the introduction into the  $\beta$ -position with respect to the chlorine atom, of any of the groups considered, *decreases* the reactivity of the chlorine atom from  $1/2$  to  $1/3$  (depending on the particular R group) of its reactivity in the unsubstituted

ethyl chloride. If the R group is introduced into the  $\gamma$ -position with respect to the chlorine, the reactivity of the chlorine is *increased* from 1.5 to nearly 3 times its original reactivity in *n*-propyl chloride. From this viewpoint there appears to be a distinct alternation in reactivity; the substituting group, when in the  $\beta$ -position, depresses the reactivity below that of the unsubstituted chloride but exalts the reactivity above that of the unsubstituted chloride when in the  $\gamma$ -position. However, the group which produces the greatest decrease in reactivity in the  $\beta$ -position does not necessarily produce the greatest exaltation when in the  $\gamma$ -position.

TABLE II  
CONFIRMATORY DATA

Compound	$\frac{RCH_2CH_2Cl}{CH_3CH_2Cl}$		Compound	$\frac{RCH_2CH_2CH_2Cl}{CH_3CH_2CH_2Cl}$	
	50°	60°		50°	60°
$C_2H_5Cl^a$	1.0	1.0	$n-C_3H_7Cl^a$	1.0	1.0
$CH_3SCH_2CH_2Cl^b$	0.62	0.85	$CH_3SCH_2CH_2CH_2Cl^b$	2.41	2.28
$C_6H_5SCH_2CH_2Cl$	.23	.33	$C_6H_5SCH_2CH_2CH_2Cl$	2.63	2.69
$C_6H_5OCH_2CH_2Cl^c$	.12	.17	$C_6H_5OCH_2CH_2CH_2Cl^c$	1.60	1.79
$C_6H_5CH_2CH_2Cl^d$	.46	.55	$C_6H_5CH_2CH_2CH_2Cl^d$	1.65	1.54
$\alpha-C_{10}H_7OCH_2CH_2Cl$	.14	.20	$\alpha-C_{10}H_7OCH_2CH_2CH_2Cl$	1.93	1.97
$\beta-C_{10}H_7OCH_2CH_2Cl$	.14	.20	$\beta-C_{10}H_7OCH_2CH_2CH_2Cl$	1.93	2.04

<sup>a</sup> Conant and Hussey, *THIS JOURNAL*, **47**, 477 (1925). <sup>b</sup> From the second paper of this series. <sup>c</sup> From the first paper of this series. <sup>d</sup> Conant and Kirner, *ibid.*, **46**, 235 (1924).

While this work was in progress a paper appeared by Bennett and Berry<sup>2</sup> in which they also made the  $\beta$ -chloro-ethyl and  $\gamma$ -chloropropyl phenyl sulfides and studied the rate of hydrolysis and also the rate of reaction with potassium iodide, using the method developed by Conant and Kirner. In the synthesis of these compounds they did not isolate the  $\omega$ -hydroxyalkyl phenyl sulfides and they claim "an attempt to distil phenyl- $\beta$ -hydroxyethyl sulfide under diminished pressure gave an unsaturated compound, probably due to the splitting out of water from the side chain, giving rise to phenyl vinyl sulfide." No mention is made of a similar attempt at the isolation of the  $\gamma$ -hydroxy compound.

We were unable to confirm the statements of Bennett and Berry regarding the instability of the  $\beta$ -hydroxyethyl phenyl sulfide. We isolated this compound as well as the  $\gamma$ -hydroxypropyl phenyl sulfide by vacuum fractional distillation at 2 mm. and used the pure hydroxy compounds for the preparation of the chlorides.

In calculating the molecular refraction, the value used for sulfur was  $n_D$  7.97 (the atomic refraction of sulfur in organic sulfides), as given by Price and Twiss.<sup>3</sup> The exaltation in the molecular refraction of com-

<sup>2</sup> Bennett and Berry, *J. Chem. Soc.*, **130**, 1676 (1927).

<sup>3</sup> Price and Twiss, *ibid.*, **101**, 1264 (1912).

pounds which have an unsaturated atom (in this case sulfur) conjugated with a double bond (in this case with a double bond in the phenyl group) as observed by Clarke and Smiles<sup>4</sup> was also found to occur in these phenylthio ethers, the exaltation averaging 0.52 unit. A similar exaltation occurred with the naphthoxyl ethers, in which oxygen is the unsaturated atom, the exaltation averaging 2.812 units.

Bennett and Berry also state that "Andrews' method for estimation of iodide in presence of chloride was found to be unsatisfactory in the present investigation owing to reaction between the iodic acid and the organic sulfide in the chloroform used for indicator. Even after removal of the organic compound the end-point with chloroform as indicator was not well defined." They therefore used the method of Lang,<sup>5</sup> which, as modified, appears to be considerably more tedious and requires both extraction with chloroform and steam distillation of each sample before titration.

In our work on these sulfur compounds we used Andrews' method of titration with the chloroform extraction recommended in previous papers. No difficulty was experienced with ill-defined end-points. The maximum deviation of the velocity constants obtained by us on the  $\beta$ -phenylthio compound was about 11% at both 50 and 60°, whereas Bennett and Berry had a deviation of 16%. Their deviation on the  $\gamma$ -compound was but 6%, whereas ours was considerably higher and there was a marked drift in the constants, particularly at 60°, which, however, is not necessarily due to errors involved in the titration. Table III indicates the excellent agreement in the absolute values of Bennett and Berry's velocity constants compared with ours despite the fact that two different methods of titration were used and by different operators. It seems to us that this agreement establishes the Andrews' method as yielding satisfactory results. Our results are calculated to 55° by the use of the temperature coefficient  $A$ .

TABLE III  
COMPARATIVE DATA

	K. and R.	$K_{55}$	B. and B.
$C_6H_5SCH_2CH_2Cl$	0.0389		0.0395
$C_6H_5SCH_2CH_2CH_2Cl$	.1798		.1434

**Vesicant Action of the Chloro Sulfides.**—A good-sized drop of the  $\beta$ -compound was placed on the right forearm with a 4 mm. glass rod and a similar drop of the  $\gamma$ -compound on the left forearm. The  $\beta$ -compound was either absorbed or evaporated more rapidly than the  $\gamma$ -compound. After about four hours a reddened area, the size of a hen's egg, developed on the right forearm due to the action of the  $\beta$ -compound. This spot

<sup>4</sup> Clarke and Smiles, *J. Chem. Soc.*, 95, 997 (1909).

<sup>5</sup> Lang, *Z. anorg. Chem.*, 122, 332 (1922).

became quite sore to the touch and after five days there was an incipient blistering of the skin. A brownish stain persisted for several months. The  $\gamma$ -compound produced no effect whatsoever.

The  $\beta$ -chloro-ethyl phenyl sulfide is thus seen to be considerably less vesicant than the  $\beta$ -chloro-ethyl methyl sulfide. The conclusions reached in the second paper of this series<sup>6</sup> were completely verified.

## Experimental

### I. The Phenylthio Series

**A. Preparation of the  $\omega$ -Phenylthio-alkyl Chlorides.**—The first member of this series, phenylthiomethyl chloride, is missing and no attempt was made to synthesize it because of previous unsuccessful attempts to prepare both its oxygen analog and methylthiomethyl chloride.<sup>7</sup>

**1. Preparation of  $\beta$ -Hydroxyethyl and  $\gamma$ -Hydroxypropyl Phenyl Sulfides.**—The most recent attempt recorded in the literature to synthesize these substances is that of Bennett and Berry,<sup>2</sup> who treated sodium thiophenoxide with ethylene and trimethylene chlorohydrin, respectively. They did not succeed in isolating these substances in a pure state and therefore did not characterize them; they merely used the crude product from the reaction mixture for another reaction. Steinkopf, Herold and Stöhr<sup>8</sup> made the  $\beta$ -hydroxy compound in a similar manner but made no attempt to isolate it.

The method used in this work was analogous to that suggested by Powell for the preparation of the oxygen analogs.<sup>9</sup> Fifty grams (0.454 mole) of thiophenol was dissolved in 180 cc. of 10% sodium hydroxide solution (0.045 mole), and then treated with slightly more than the theoretical amount of the desired chlorohydrin. The reaction took place rapidly and the mixture was refluxed for half an hour to insure its completion. The oily layer was separated, the aqueous layer extracted twice with ether and the combined oil-ether layer washed with water and dried over anhydrous sodium sulfate. The ether was distilled off, leaving a practically quantitative yield of nearly pure product which was carefully fractionated several times under reduced pressure from a Claisen fractionating flask. Phenyl  $\beta$ -hydroxyethyl sulfide is a water-white liquid with a rather sweet, not unpleasant odor.

*Anal.* Subs., 0.2160: BaSO<sub>4</sub>, 0.3241. Calcd. for C<sub>8</sub>H<sub>10</sub>OS: S, 20.79. Found: S, 20.61.

There was no difficulty whatsoever experienced during the fractional vacuum distillation and there was no evidence of unsaturated compound formation as reported by Bennett and Berry. They did not state at what pressure their distillation was carried out, but at 1–2 mm. the above hydroxy compound distills smoothly and without decomposition and yields a pure product, as indicated by the analysis.

Phenyl  $\gamma$ -hydroxypropyl sulfide is a water-white liquid.

*Anal.* Subs., 0.1808: BaSO<sub>4</sub>, 0.2490. Calcd. for C<sub>9</sub>H<sub>12</sub>OS: S, 19.06. Found: S, 18.91.

**2. Preparation of  $\beta$ -Chloro-ethyl and  $\gamma$ -Chloropropyl Phenyl Sulfides.**—The  $\beta$ -chloro-ethyl compound was first prepared by Steinkopf and co-workers<sup>8</sup> by passing hy-

<sup>6</sup> Kirner, *THIS JOURNAL*, **50**, 2449 (1928).

<sup>7</sup> Kirner, *ibid.*, **48**, 2747 (1926); **50**, 2451 (1928).

<sup>8</sup> Steinkopf, Herold and Stöhr, *Ber.*, **53**, 1012 (1920).

<sup>9</sup> Powell, *THIS JOURNAL*, **45**, 2709 (1923); Kirner, *ibid.*, **48**, 2748 (1926).

drogen chloride into the crude hydroxy compound. They give the boiling point as 144.5° at 26 mm. and 245° at atmospheric pressure; yield, 76%. Lecher and Stöcklin<sup>10</sup> also obtained it in good yield by the addition of phenyl sulfur chloride to ethylene. They give the boiling point as 122° at 13 mm. and mention the vesicant action of the compound. Bennett and Berry made both the  $\beta$ -chloro-ethyl and  $\gamma$ -chloropropyl compounds by the application of Darzens' reaction to the corresponding hydroxy compounds. They give the boiling point of the  $\beta$ -chloro-ethyl compound as 117° at 12 mm. and the boiling point of the  $\gamma$ -chloropropyl compound as 137° at 13 mm.; they state that the ethyl compound has a very slight vesicant action and that the propyl compound is not appreciably vesicant.

In this work the alcohols previously described were converted into the chlorides by Darzens' method,<sup>11</sup> using thionyl chloride and pyridine. Twenty grams of the alcohol was treated with the theoretical amount of pyridine and about a 25% excess of thionyl chloride was added dropwise. The characteristic precipitate appeared after about half of the thionyl chloride had been added but redissolved on further addition, forming two layers. The sulfur dioxide was removed by heating on a steam-bath. The yield of crude product was quantitative and the yield after several vacuum fractionations was 80–85%.

$\beta$ -Chloro-ethyl phenyl sulfide is a colorless liquid.

*Anal.* Subs., 0.1460, 0.2172: BaSO<sub>4</sub>, 0.1983, 0.2925. Calcd. for C<sub>9</sub>H<sub>9</sub>SCl: S, 18.58. Found: S, 18.65, 18.50.

$\gamma$ -Chloropropyl Phenyl Sulfide.—*Anal.* Subs., 0.2014, 0.2066: BaSO<sub>4</sub>, 0.2525, 0.2565. Calcd. for C<sub>9</sub>H<sub>11</sub>SCl: S, 17.18. Found: S, 17.20, 17.06.

The physical constants of the phenyl sulfides are given in Table IV.

TABLE IV  
PHYSICAL CONSTANTS OF PHENYL SULFIDES

Phenyl sulfide	B. p., °C.	$d_{20}^{20}$	$d_4^{20}$	$n_D^{20}$	$M_D$		Exaltation
					Calcd.	Obs.	
$\beta$ -Hydroxyethyl	115–116 (2 mm.)	1.1451	1.1431	1.5917	45.038	45.611	0.573
$\gamma$ -Hydroxypropyl	134–135 (2 mm.)	1.1197	1.1178	1.5813	49.656	50.158	.502
$\beta$ -Chloro-ethyl	100–101 (4 mm.)	1.1829	1.1808	1.5838	48.380	48.904	.524
$\gamma$ -Chloropropyl	116–117 (4 mm.)	1.1556	1.1536	1.5752	52.998	53.471	.473

## B. Reaction Velocity Measurements

TABLE V  
REACTION BETWEEN  $\beta$ -CHLORO-ETHYL PHENYL SULFIDE AND POTASSIUM IODIDE (WITH EXTRACTION)

Time, hours	At 50°		Time, hours	At 60°	
	Reacted, %	K		Reacted, %	K
12.70	11.67	0.0215	6.0	16.33	0.0656
24.0	22.46	.0236	12.5	30.43	.0652
49.3	40.17	.0237	12.85	31.49	.0661
76.0	54.26	.0238	18.50	42.18	.0674
100.33	64.34	.0242	25.50	49.59	.0618
			35.75	60.17	.0602
	Mean	.0234	50.10	72.29	.0611
				Mean	.0639

<sup>10</sup> Lecher and Stöcklin, *Ber.*, **53**, 414 (1925).

<sup>11</sup> Darzens, *Compt. rend.*, **152**, 1314 (1911).

TABLE V (Concluded)

REACTION BETWEEN  $\alpha$ -CHLOROPROPYL PHENYL SULFIDE AND POTASSIUM IODIDE  
(WITH EXTRACTION)

Time, hours	At 50°		Time, hours	At 60°	
	Reacted, %	K		Reacted, %	K
2.50	13.17	0.124	1.0	15.50	0.372
5.25	25.52	.125	2.0	24.56	.314
11.0	42.55	.115	4.0	40.77	.298
15.0	52.15	.114	7.5	57.94	.269
20.0	59.58	.106	11.5	67.07	.228
26.5	67.30	.100	17.10	75.68	.198
	Mean	.114		Mean	.280

## II. The $\alpha$ -Naphthoxyl Series

A. Preparation of the  $\omega$ -Chloro-alkyl  $\alpha$ -Naphthyl Ethers.—The first members of both the  $\alpha$ - and  $\beta$ -series are unknown and their synthesis was not attempted.

1. Preparation of  $\beta$ -Hydroxyethyl and  $\gamma$ -Hydroxypropyl  $\alpha$ -Naphthyl Ethers.—The  $\beta$ -hydroxyethyl ether was first prepared by Boyd and Marle<sup>12</sup> by treatment of ethylene oxide with sodium  $\alpha$ -naphthoxide. They give the melting point as 42°. In this work these substances were made analogously to the method used for the preparation of the phenylthio ethers described above. The reactions go rapidly, the emulsion appearing in about ten minutes and the reaction appears to be completed a few minutes later. The mixture is worked up in the usual way; it was found necessary to carry out several extractions of the oily ether layer with 5% sodium hydroxide solution to remove excess  $\alpha$ -naphthol.

$\beta$ -Hydroxyethyl  $\alpha$ -naphthyl ether boiled at 167° at 2 mm. It had a light yellow color. Numerous attempts were made to crystallize it from various solvents, simple and mixed, but they all failed. On long standing in an ice box the oil started to crystallize but the best melting point obtainable was 22–24°. It is possible that some decomposition occurred during distillation which caused the melting point to be so much lower than that reported by Boyd and Marle.

$\gamma$ -Hydroxypropyl  $\alpha$ -naphthyl ether is a new compound. It was crystallized from petroleum ether, giving a pure white mass of needle-shaped rosetts; m. p. 65.5–66.5°; yield (crude), 79%.

*Anal.* Subs., 0.2082: CO<sub>2</sub>, 0.5894; H<sub>2</sub>O, 0.1362. Calcd. for C<sub>13</sub>H<sub>14</sub>O<sub>2</sub>: C, 77.19; H, 6.98. Found: C, 77.27; H, 7.32.

2. Preparation of  $\beta$ -Chloro-ethyl and  $\gamma$ -Chloropropyl  $\alpha$ -Naphthyl Ethers.—Clemo and Perkin<sup>13</sup> first made the  $\beta$ -chloro-ethyl compound by the direct introduction of the chloro-ethyl group into  $\alpha$ -naphthol, using  $\beta$ -chloro-ethyl *p*-toluenesulfonate. They give the melting point as 28° and the boiling point as 202° at 16 mm. We obtained this compound by carrying out a Darzens reaction on the corresponding alcohol, using pyridine and thionyl chloride. The sulfur dioxide was removed by heating on a water-bath for two hours; yield of crude product, 85%. This was carefully fractionated three times in a vacuum, giving a 61% yield of highly purified material.  $\beta$ -Chloro-ethyl  $\alpha$ -naphthyl ether is a rather viscous, yellow oil which did not crystallize.

<sup>12</sup> Boyd and Marle, *J. Chem. Soc.*, 105, 2135 (1914).

<sup>13</sup> Clemo and Perkin, *ibid.*, 121, 646 (1922).

*Anal.* Subs., 0.2718: AgCl, 0.1891. Calcd. for  $C_{12}H_{11}OCl$ : Cl, 17.16. Found: Cl, 17.21.

$\gamma$ -Chloropropyl  $\alpha$ -naphthyl ether is a new compound. It was prepared by the method just described; yield of twice distilled product, 54%. The compound is a light yellow, viscous liquid which did not crystallize.

*Anal.* Subs., 0.3034: AgCl, 0.1996. Calcd. for  $C_{13}H_{13}OCl$ : Cl, 16.07. Found: Cl, 16.27.

The physical constants of the  $\alpha$ -naphthyl ethers are given in Table VI.

TABLE VI  
PHYSICAL CONSTANTS OF  $\alpha$ -NAPHTHYL ETHERS

$\alpha$ -Naphthyl ether	B. p., ° C.	$d_{20}^{20}$	$d_4^{20}$	$n_D^{20}$	$M_D$		Exaltation
					Calcd.	Found	
$\beta$ -Hydroxyethyl	167° (2 mm.), m. p. 22-24°						
$\gamma$ -Hydroxypropyl	65.5-66.6 (m. p.)						
$\beta$ -Chloro-ethyl	145-147(1.5 mm.)	1.1993	1.1972	1.6139	57.391	60.122	2.731
$\gamma$ -Chloropropyl	167-168(1 mm.)	1.1686	1.1665	1.6025	62.009	64.903	2.894

## B. Reaction Velocity Measurements

TABLE VII

REACTION BETWEEN  $\beta$ -CHLORO-ETHYL  $\alpha$ -NAPHTHYL ETHER AND POTASSIUM IODIDE

At 50°			At 60°		
Time, hours	Reacted, %	K	Time, hours	Reacted, %	K
25.1	14.00	0.0132	13.0	18.84	0.0356
25.1	13.33	.0126	24.33	35.61	.0409
50.05	26.92	.0140	38.55	49.76	.0411
75.0	37.44	.0142	50.0	58.90	.0415
100.5	46.05	.0141	66.7	67.60	.0400
	Mean	.0136		Mean	.0398

REACTION BETWEEN  $\alpha$ -CHLOROPROPYL  $\alpha$ -NAPHTHYL ETHER AND POTASSIUM IODIDE

At 50°			At 60°		
Time, hours	Reacted, %	K	Time, hours	Reacted, %	K
3.0	11.50	0.0895	1.0	8.17	0.187
7.25	23.88	.0838	2.0	17.44	.212
12.50	37.48	.0851	4.0	31.45	.212
15.75	44.24	.0847	6.0	43.76	.219
20.50	51.55	.0815	8.0	52.31	.214
30.90	63.39	.0764	11.25	61.01	.196
	Mean	.0835	15.10	71.36	.197
				Mean	.205

## III. The $\beta$ -Naphthoxyl Series

### A. Preparation of the $\omega$ -Chloro-alkyl $\beta$ -Naphthyl Ethers

1. Preparation of  $\beta$ -Hydroxyethyl and  $\gamma$ -Hydroxypropyl  $\beta$ -Naphthyl Ethers.—This  $\beta$ -hydroxyethyl ether was also made by Boyd and Marle. They give the melting point as 76°. Rindfus, Ginnings and Harnack<sup>14</sup> made it by treatment of sodium  $\beta$ -

<sup>14</sup> Rindfus, Ginnings and Harnack, *THIS JOURNAL*, **42**, 164 (1920).



naphthoxide with ethylene chlorohydrin; m. p. 76–77°. We obtained it using precisely the same method that was used for the  $\alpha$ -isomer. Crystallization from a mixture of one part of benzene and two parts of petroleum ether gave a product melting at 75–76°; yield of pure product, 57%.

The  $\gamma$ -hydroxypropyl ether was also prepared by Rindfusz and co-workers with a 25% yield; m. p. 99–99.5°. We found the preparation of this compound to go more slowly than the ethyl ether. Crystallization from a mixture of benzene and petroleum ether gave the pure product melting at 98.7–99.4°; yield, 38%.

2. Preparation of  $\beta$ -Chloro-ethyl and  $\gamma$ -Chloropropyl  $\beta$ -Naphthyl Ethers.—Clemon and Perkin also made this chloro-ethyl ether. A quantitative yield of crude product was obtained. The pure crystallized compound melted at 83°. We obtained the compound by the Darzens reaction on the alcohol, the crude product also being obtained in quantitative yield. Repeated crystallization from 95% alcohol gave a pure product melting at 80–81°.

*Anal.* Subs., 0.3217: AgCl, 0.2199. Calcd. for  $C_{12}H_{11}OCl$ : Cl, 17.16. Found: Cl, 16.91.

$\gamma$ -Chloropropyl  $\beta$ -naphthyl ether is a new compound and was made by the procedure already described; the yield of crude product was 96%. Crystallization from absolute alcohol gave pure white crystals melting at 47–47.5°.

*Anal.* Subs., 0.3020: AgCl, 0.1966. Calcd. for  $C_{13}H_{13}OCl$ : Cl, 16.07. Found: Cl, 16.10.

## B. Reaction Velocity Measurements

TABLE VIII

REACTION BETWEEN  $\beta$ -CHLORO-ETHYL  $\beta$ -NAPHTHYL ETHER AND POTASSIUM IODIDE

At 50°			At 60°		
Time, hours	Reacted, %	K	Time, hours	Reacted, %	K
16.0	9.50	0.0137	13.0	20.77	0.0398
26.0	15.43	.0142	24.5	34.72	.0393
50.1	27.30	.0142	35.5	45.10	.0386
75.0	36.20	.0136	49.2	55.49	.0382
100.5	43.62	.0130	67.6	64.39	.0359
	Mean	.0137		Mean	.0384

REACTION BETWEEN  $\gamma$ -CHLOROPROPYL  $\beta$ -NAPHTHYL ETHER AND POTASSIUM IODIDE

At 50°			At 60°		
Time, hours	Reacted, %	K	Time, hours	Reacted, %	K
5.0	17.92	0.0874	2.0	18.57	0.228
10.1	32.52	.0876	4.0	32.87	.224
15.6	43.69	.0840	6.75	48.07	.223
25.25	56.48	.0766	8.0	51.54	.209
	Mean	.0839	10.4	59.18	.201
			15.0	69.51	.188
				Mean	.212

## Summary

1. The effect of the phenylthio and  $\alpha$ - and  $\beta$ -naphthoxyl groups upon the reactivity of a chlorine atom in the  $\beta$ - and  $\gamma$ -positions has been determined by studying the velocity with which the chlorine is replaced

by iodine using potassium iodide in absolute acetone solution. A comparison was made of the effect of these groups with the methylthio, phenoxyl and phenyl groups when similarly situated.

2.  $\beta$ -Chloro-ethyl phenyl sulfide was found to have only a weak vesicant action and the  $\gamma$ -chloropropyl phenyl sulfide was completely non-vesicant.

3. The following substances were isolated and characterized for the first time:  $\beta$ -hydroxyethyl phenyl sulfide,  $\gamma$ -hydroxypropyl phenyl sulfide,  $\gamma$ -hydroxypropyl  $\alpha$ -naphthyl ether,  $\gamma$ -chloropropyl  $\alpha$ -naphthyl ether,  $\gamma$ -chloropropyl  $\beta$ -naphthyl ether.

HOUSTON, TEXAS

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[A COMMUNICATION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

### COMPETITIVE HYDROGENATIONS

BY HOMER ADKINS, F. F. DIWOKY AND A. E. BRODERICK

RECEIVED MAY 27, 1929

PUBLISHED NOVEMBER 8, 1929

The importance of precise information on the relation of the structure of a compound to its reactivity as manifested in the ease of reduction led Vavon and Husson<sup>1</sup> to devise a unique method for the experimental study of the rate of reduction of certain derivatives of cinnamic acid. Their method consisted in adding one mole of hydrogen to a mixture of one mole of *d*- $\alpha$ -pinene and one mole of the compound under consideration, and then calculating the distribution of the hydrogen between the two compounds from the change in optical activity of the mixture. They assumed that the distribution of the hydrogen between the pinene and the unsaturated compounds was a measure of the ease of reduction of the unsaturated compounds. If, for example, cinnamic acid took up 57% of the hydrogen (pinene 43%) and  $\alpha$ -methylcinnamic acid took up 26% (pinene 74%), they concluded that cinnamic acid was reduced much more easily than the substituted acid. This method of comparison has two very considerable advantages over the usual one of noting the rate of absorption of hydrogen by a single compound. The latter method for an accurate comparison demands that the comparisons be made over catalysts of identical activity. This is a condition which it is difficult if not impossible to meet if an extended list of compounds is to be compared. This method also presupposes that there is no impurity in any of the compounds which would lower the activity of the catalyst. An attempt was made to repeat and extend their work because of our interest in simultaneous reactions and because previous work in this Laboratory made it seem probable that the ratio of the distribution would be a func-

<sup>1</sup> Vavon and Husson, *Compt. rend.*, **176**, 989 (1923).